

Thermosensitive Nanocables Prepared by Surface-Initiated Atom Transfer Radical Polymerization

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Abstract Thermosensitive nanocables consisting of Au nanowire cores and poly(*N*-isopropylacrylamide) sheaths (denoted as Au/PNIPAAm) were synthesized by surface-initiated atom transfer radical polymerization (SI-ATRP). The formation of PNIPAAm sheath was verified by Fourier transform infrared (FTIR) and hydrogen nuclear magnetic resonance (^1H NMR) spectroscopy. Transmission electron microscope (TEM) results confirmed the core/shell structure of nanohybrids. The thickness and density of PNIPAAm sheaths can be adjusted by controlling the amount of cross-linker during the polymerization. Signature temperature response was observed from Au/cross-linked-PNIPAAm nanocables. Such smart nanocables show immense potentials as building blocks for novel thermosensitive nanodevices in future.

Keywords Nanocables · Gold nanowires · Poly(*N*-isopropylacrylamide) · Surface-initiated atom transfer radical polymerization · Thermoresponsive

Introduction

Coaxial nanocables have received extensive attentions since they were first prepared in 1997 [1]. In general, they comprise a nanowire core and a protective shell. Based on the nature of sheath materials, different synthetic routes are developed to prepare diverse core/shell nanocables.

Roughly speaking, sheath materials can be divided into two groups: hard sheaths (e.g. C [2], SiO_2 [3], BN [4], CdSe [5], Au [6]) and soft sheaths (mainly polymers [7]). The main methods to form a hard or inorganic sheath are vapor transfer-based [8, 9] or electrochemical deposition [10], but the coating of nanowires with soft or organic sheaths, especially polymeric shells, needs much milder solution-based reactions. Polymeric sheaths are advantageous over inorganic sheaths in making insulated nanocables, which is essential in optoelectronic nanodevices fabrication and high-density microcircuit industry in order to separate different signal circuit. Moreover, the polymeric coatings would add multiple functions to nanocables, for example, the pH-, temperature- and ion strength-responsive properties, allowing the potential applications in smart nanomachines. Furthermore, polymeric sheaths facilitate a wide range of surface functionalization possibilities, such as biomolecule immobilization. Finally, many polymeric coatings are biocompatible, which promotes the introduction of the one-dimensional (1D) inorganic nanostructures into the biological systems.

The surface functionalization of nanowires with polymeric sheaths can be achieved via several routes: (1) “grafting” method. The as-prepared nanowires are used as templates to graft a polymeric coating. For example, Au/polystyrene (PS) cable-like structures were obtained via emulsion polymerization on as-prepared Au nanorods [11]; Ag nanofibers/PS nanocomposites were prepared by using the reverse micelle-gas antisolvent-ultrasound method [12]. (2) “filling” method. Nanocables can be synthesized by filling core materials into existing polymeric or self-assembled peptide nanotubes [13]. However, the fabrication of a polymeric nanotube template with desired diameter and length is quite challenging. (3) in situ formation. In this protocol, the nanowire cores and outlayers

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are formed simultaneously through a one-pot solution reaction. For instance, CdSe/poly(vinyl acetate) (PVAc) nanocables were synthesized from a heterogeneous system of vinyl acetate (VAc) monomer and precursor under γ -irradiation at room temperature [14]; Ag/poly(vinyl alcohol) (PVA) [15], Te/PVA [16] and Pd/PVA [17] nanocables were prepared via one-step hydrothermal process. Besides, novel approaches including electrospinning [18], self-assembly of nanoparticles [19], and interfacial reaction [20] are also developed to prepare various nanocable structures.

Recently, surface-initiated atom transfer radical polymerization (SI-ATRP) has been demonstrated as a useful tool for coating different substrates with polymeric outlayers [21]. However, there have been very few reports on the preparation of metal/polymer nanocables via SI-ATRP. John Arnold and Peidong Yang and et al. reported the synthesis of Si/SiO₂/poly(methyl methacrylate) (PMMA) nanocables via SI-ATRP [22]. John Arnold and co-workers further applied this method to fabricate ZnO/PMMA and ZnO/PS nanocables [23]. Moreover, except conducting polymers [24], few other types of functional polymeric sheaths have been integrated onto nanowire cores.

Poly(*N*-isopropylacrylamide) (PNIPAAm) is a widely used thermosensitive polymer which undergoes a coil-globule transition at the lower critical solution temperature (LCST) around 32 °C [25]. PNIPAAm coatings have been successfully grafted via SI-ATRP on gold nanoparticles [26–28], gold nanorods [29], silica beads [30], dextran particles [31], carbon nanotubes [32] and self-assembled peptide nanotubes [33]. The coating of high aspect ratio 1D nanowires with PNIPAAm sheaths, however, has not been demonstrated and could be a novel kind of stimulation responsive materials.

Here, we report the synthesis of thermosensitive nanocables by the SI-ATRP method. Gold nanowires (Au NWs) of 1.5–1.8 μm in length were prepared as the templates via a modified seeding growth method developed by our team. Two different sorts of PNIPAAm sheaths (non-cross-linked and cross-linked) were directly grafted from the Au NW surface through the surface-initiated polymerization. The smart thermosensitive nanocables would become the fundamental materials for fabricating resistance sensitive/thermo sensitive nanodevices in future.

Experimental

Materials

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH_4), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA)

and L-ascorbic acid (AA) were used as received. NIPAAm monomer was purchased from Aldrich and purified by recrystallization with hexane. $\text{Cu}^{\text{I}}\text{Br}$ was purified by dissolution in HBr and recrystallization done with water/ethanol. Deionized water was distilled twice again before use. All the glasswares were washed by aqua regia and repeatedly purified thrice by distilled water. The disulfide initiator $[\text{BrC}(\text{CH}_3)_2\text{COO}(\text{CH}_{11}\text{S})_2]$ was prepared according to the literature [34].

Synthesis of Au NWs

Au NWs of 1.5–1.8 μm in length were synthesized by a pH-controlled growth method which has been developed by our team recently [35]. In brief, the Au seed solution was prepared by mixing 5.0 mL 0.20 M CTAB with 5.0 mL of 0.50 mM HAuCl_4 . A quantity of 0.60 mL freshly prepared ice-cold NaBH_4 (0.010 M) was added all at once under vigorous stirring. The stirring was continued for 2 min and the seed solutions were used within 2–4 h after their preparation.

The growth solution was prepared by adding 10 mL 0.30 M CTAB to the same volume of 1.0 mM HAuCl_4 and 140 μL 0.10 M AA. After that, 0.30 mmol HCl was injected into the growth solution to lower the solution pH value to around 2.5. Finally, 24 μL seed solution were added rapidly, followed by gently mixing for about 1 min. The solution was then kept in 25 °C water bath overnight.

Preparation of Thermosensitive Nanocables

The first step of preparing PNIPAAm capped nanocables is to immobilize the disulfide-terminated initiator onto the surface of Au NWs. Excess surfactant in nanowire solution was removed by slow centrifugation (1,500 rpm, 15 min). After purification, 1.135 mL initiator/THF solution (0.02 mmol) was added dropwise to Au NWs. The site exchange reaction was left to proceed overnight before centrifugation. The precipitate was collected and washed by $\text{H}_2\text{O}/\text{DMF}$ (*v*: *v* = 1:1) and THF, respectively. Finally, the initiator-capped Au NWs were redispersed in 8 mL $\text{H}_2\text{O}/\text{DMF}$ (*v*: *v* = 1:1) solution.

For the formation of noncross-linked and cross-linked PNIPAAm shells on Au NWs, the above Au NWs at initiator solution (8 mL) was equally divided into two separate round-bottomed flasks (labelled with I and II). Then, 0.4526 g NIPAAm (4 mmol) and 10.0 μL PMDETA (0.04 mmol) were added to each flask. In flask II, 62 μL ethylene diacrylate (10 mol% with respect to NIPAAm) was added as the cross-linker. The mixture was degassed by three freeze-pump-thaw cycles with N_2 . Degassed $\text{Cu}^{\text{I}}\text{Br}$ (5.7 mg, 0.04 mmol) was finally added to both systems to initiate the polymerization. The reaction was

performed for 48 h and was terminated by opening the system to air. The nanocables were separated from the reaction solution by centrifugation. After repeating wash, centrifugation and redispersion, the samples were dispersed in water finally.

Characterizations

FTIR spectra were recorded by using a Bruker Vectors 22 instrument. ^1H NMR measurements were carried out on a DMX500 spectrometer (Bruker). TEM images of Au NWs and nanocables were obtained by using a JEM-1200EX transmission electron microscope. The nanocables were stained for TEM observation on copper grids by using 1.5% phosphotungstic acid. The transmittance of nanocables solution was measured on a Shimadzu UV-2550 spectrometer. A water bath was used to control the temperature of nanocable solutions.

Results and Discussions

The process of preparing Au/PNIPAAm nanocables is illustrated in Scheme 1. Two steps including the immobilization of disulfide initiator and surface polymerization are involved. The incorporation of initiator and PNIPAAm sheath was verified by FTIR spectra (Fig. 1). As-synthesized Au NWs have a characteristic absorbance at $1,481\text{ cm}^{-1}$, corresponding to the C–H antisymmetric methylene scissoring mode of $\text{CH}_3\text{-N}^+$ moiety in CTAB capping molecules [36]. After ligand exchange with disulfide initiator, a new characteristic absorbance at $1,735\text{ cm}^{-1}$ appears. This peak can be attributed to the C=O stretching from the bromoester moiety of the polymerization initiator [26, 27], indicating the successful immobilization of initiator molecules on Au NWs. The FTIR spectra also show the characteristic peaks of Au/PNIPAAm nanocables at $1,645\text{ cm}^{-1}$ (C=O stretching, amide I), and $1,552\text{ cm}^{-1}$ (N–H bending, amide II) which proves the formation of PNIPAAm sheaths [26, 27].

The generation of PNIPAAm sheath can be further determined by ^1H NMR spectra (Fig. 2). Au NWs and Au/PNIPAAm nanocables were separated from H_2O by centrifugation at 1,500 rpm for 15 min and redispersed in

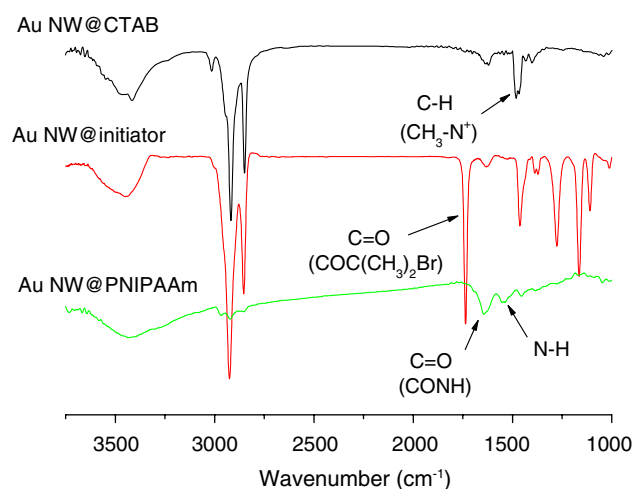


Fig. 1 FTIR spectra of as-prepared Au NWs, initiator-capped Au NWs and Au/PNIPAAm nanocables

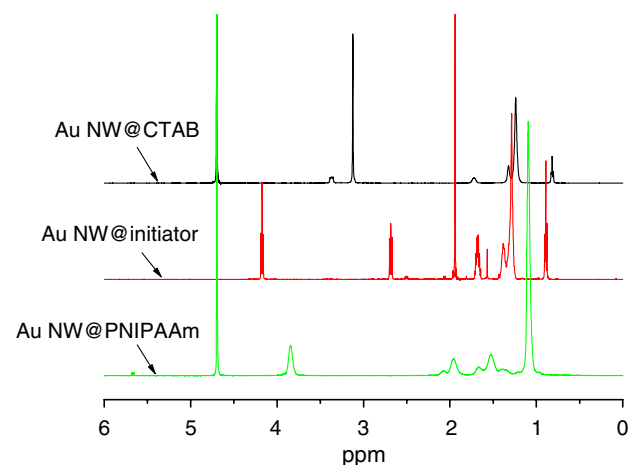
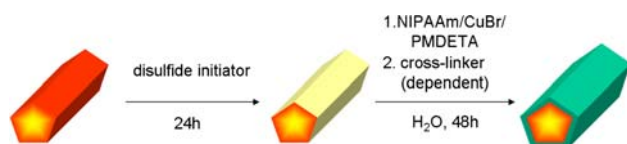


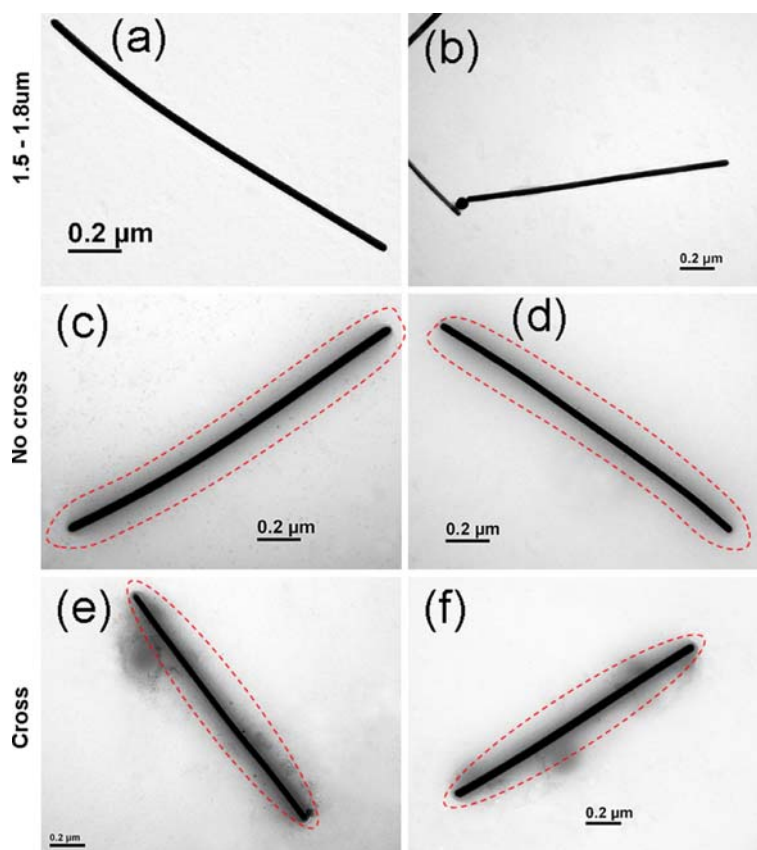
Fig. 2 ^1H NMR spectra of as-prepared Au NWs, initiator-capped Au NWs and Au/PNIPAAm nanocables

D_2O . Initiator modified Au NWs were redispersed in CDCl_3 instead. The as-prepared Au NWs showed alkane signal of CTAB at 3.37 (2H, $\alpha\text{-CH}_2$), 1.72 (2H, $\beta\text{-CH}_2$), 1.32 (6H, $\gamma\text{-CH}_2$ of $(\text{CH}_2)_3$), 1.24 (20H, $(\text{CH}_2)_{10}$, main chain peak) and 0.82 (3H, $\omega\text{-CH}_3$) ppm [37]. And the large narrow *N*-methyl (headgroup, 9H) singlet appeared at 3.12 ppm [37]. After capping with disulfide initiator, new peaks at 4.17 (t, 2H, OCOCH_2), 2.69 (q, 2H, SCH_2) and 1.94 (s, 6H, CH_3) ppm which belong to the disulfide initiator [34, 38] appeared while the characteristic peak of CTAB at 3.12 ppm was hard to be detected. The change in ^1H NMR spectra indicates the replacement of CTAB-capping molecules with disulfide initiator after site exchange reaction. Au/PNIPAAm nanocables displayed characteristic PNIPAAm signals at 3.84 (CH, side chain), 1.96



Scheme 1 Two-step synthesis of Au/PNIPAAm nanocables. The red: Au NWs; the light yellow coating: initiator layer; the dark green coating: PNIPAAm sheath

Fig. 3 TEM images of (a, b) as-prepared Au NWs, (c, d) Au/noncross-linked PNIPAAm nanocables and (e, f) Au/cross-linked PNIPAAm nanocables. The nanocable samples were stained by phosphotungstic acid before TEM observation. All scale bars are 0.2 μm



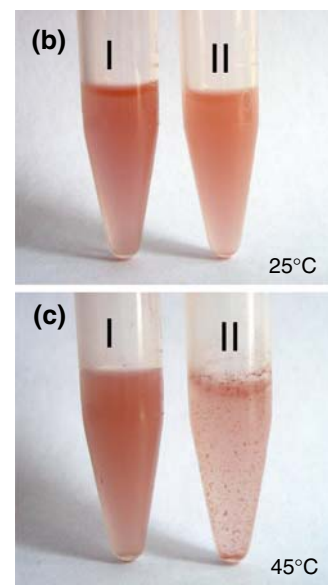
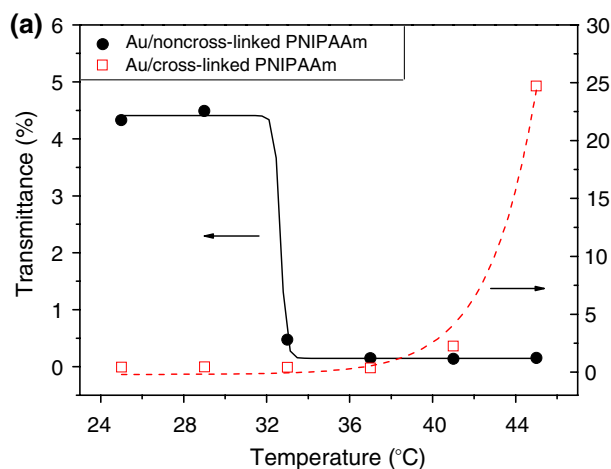
(CH, main chain), 1.53 (CH₂, main chain) and 1.09 (CH₃, side chain) ppm, thus verifying the successful coating of PNIPAAm sheath [32]. The ¹H NMR spectra are in good agreement with FTIR results, both indicating the attachment of PNIPAAm chains onto the surface of Au NWs.

The core/shell coaxial structure was directly observed by TEM (Fig. 3). The first row in Fig. 3 (Fig. 3a, b) shows the TEM images of as-prepared Au NWs, 1.5–1.8- μm long and 40-nm wide. The second row (Fig. 3c, d) and third row (Fig. 3e, f) are typical TEM images of Au/noncross-linked PNIPAAm and Au/cross-linked PNIPAAm nanocables, respectively. The dark Au NWs were found to be localized at the centre of a gray PNIPAAm halo. The polymeric sheaths were quite uniform judged by the TEM images and the thickness was estimated to be about 50 nm when no cross-linker was used (Fig. 3c, d). In contrast, appropriate amount of cross-linker would slightly increase the thickness of PNIPAAm coating to about 55 nm. The cross-linked sheaths also appeared much darker in TEM images (Fig. 3e, f), which could be due to the higher density of polymer chains than the noncross-linked ones. Such core/shell structure is identical to the previous reports of Si/SiO₂/PMMA [22], ZnO/PMMA and ZnO/PS [23].

The thermosensitive properties of Au/PNIPAAm nanocables were characterized by UV spectrometer. Figure 4a shows the variations of the transmittance of

nanocable solution when exposed to different temperatures. Interestingly, the Au/noncross-linked nanocables and Au/cross-linked nanocables exhibited completely different temperature-sensitive properties. The transmittance of Au/noncross-linked nanocables decreases with the increase of temperature (Fig. 4a). At the range of 32–34 °C, a sharp transition occurred due to the inherent hydrophilic-to-hydrophobic transition of PNIPAAm [25]. The decrease in transmittance in high-temperature range may be attributed to the formation of large nanocable aggregates, which significantly enhanced the scattering intensity of the solution. Our observation is also in good agreement with the former reports of PNIPAAm-capped gold nanoparticles [39]. However, the transmittance of Au/cross-linked PNIPAAm nanocables gradually increased when the temperature was higher than 36 °C and was nearly 50 times higher than the noncross-linked ones at 45 °C (Fig. 4a). Digital photos also showed the difference of thermosensitive properties of Au/noncross-linked (I in Fig. 4b, c) and Au/cross-linked PNIPAAm nanocables (II in Fig. 4b, c). At room temperature (25 °C), the two kinds of PNIPAAm-coated nanocables did not show significant difference (Fig. 4b). When the temperature increased to 45 °C, noncross-linked nanocables did not change much (Fig. 4c, I) although the UV-vis spectra showed us the happening of a possible aggregation. On the contrary, the

Fig. 4 a Thermoresponsive changes in transmittance of Au/noncross-linked PNIPAAm (circles) and Au/cross-linked PNIPAAm (squares); Digital photos of Au/noncross-linked PNIPAAm (number I) and Au/cross-linked PNIPAAm (number II) nanocables at **b** 25 °C and **c** 45 °C, respectively



cross-linked nanocables experienced a significant precipitation through the temperature increasing cycle (Fig. 4c, II). The aqueous media thus was much more transparent, which results in an atypical transmittance increase with an increase in temperature. We hypothesized that the cross-linked PNIPAAm sheaths with higher density would become more hydrophobic so that more serious aggregation occurred. It hence provides a method to effectively tune the thermoresponsive properties of Au/PNIPAAm nanocables solely by adjusting the amount of cross-linker used.

Conclusions

In summary, two types of thermosensitive Au/PNIPAAm nanocables were successfully prepared via SI-ATRP method. FTIR, ^1H NMR and TEM results clearly demonstrate the formation of PNIPAAm sheath. The use of cross-linker in the polymerization process improved the density and thickness of the polymeric shell as estimated from the TEM images. The different thermoresponsive properties of Au/noncross-linked PNIPAAm and Au/cross-linked PNIPAAm nanocables were determined by transmittance measurement. These kinds of thermosensitive nanocables provide potential applications in resistance sensitive/thermosensitive nanodevices, smart drug delivery and other stimuli-responsive devices.

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